

# PATENT ABSTRACTS OF JAPAN

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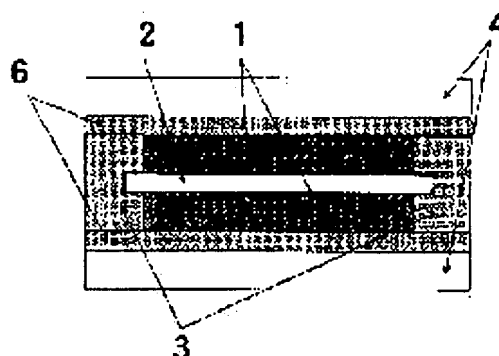
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## (54) CONDUCTIVE FILM FOR CURRENT COLLECTOR

### (57)Abstract:

**PROBLEM TO BE SOLVED:** To provide such mechanical strength as breakage or disconnection does not take place at thermo-compression bonding by adding a specific conductive agent by specified pts.wt. to a specific resin wherein gel percentage has specific bridge structure, for specified specific resistance of a conductive resin layer.

**SOLUTION:** Related to a conductive film 6, a conductive resin layer is laminated on a metal film. As a base resin of the conductive resin, urethane, acrylic, polyester, vinyl acetate, etc., are used, and bridged, with a gel percentage being 90% or more. The specific resistance of the conductive resin is 1  $\Omega$ .cm or less. The conductive agent is the powder or fiber of carbon black, Cu, Zn, and Au, added by 10-500 pts.wt. relative to a resin 100 pts.wt. The metal film in a current collector is Al or Cu, with the thickness of the metal film being 10-30  $\mu$ m.



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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] the current collection to which the solid content polarity electrode which uses this invention for the electric double layer capacitor which used the drainage system electrolytic solution is stuck -- the body and its function -- the current collection for acquiring the contact condition and conductivity which were stabilized about the conductive film with reduction of the contact resistance especially to a polarizable electrode and an electrode plate -- the body and its function -- it is related with a conductive film.

[0002]

[Description of the Prior Art] As shown in drawing 1, the fundamental configuration of an electric double layer capacitor lays the polarizable electrode of a pair underground through a porous separator inside an obturation frame, seals this polarizable electrode with a metal-electrode plate, and is formed. However, in this case, it is only in contact, a poor contact occurs partially, and a polarizable electrode and a metal-electrode plate have a possibility of causing the increment in internal resistance. In order to solve this, as shown in drawing 2, between a polarizable electrode and metal-electrode plates is pasted up with electroconductive glue, or pasting up by thermocompression bonding through a conductive thermoplastic film, as shown in drawing 3 is proposed.

[0003] However, when pasting up a polarizable electrode and a metal-electrode plate with electroconductive glue, the effect of the hardening condition of electroconductive glue or a residual solvent showed uneven conductivity in many cases, the increase of contact resistance and the rise of internal resistance were caused on the contrary, and there was a problem that a high current could not be taken out. moreover, in using the conventional conductive thermoplastic film To the configuration resin of a film, polypropylene, polyethylene, a polyvinyl chloride, In order to use thermoplastics, such as polystyrene, polyurethane, a polyamide, and polyimide, to make this resin distribute carbon black and to film-ize using the conventionally well-known shaping approaches, such as an extrusion method and the calender rolling-out method, When the content of an electric conduction agent increased, the moldability was remarkably inferior, and when the reinforcement of the film itself also became very weak and lessened the content of an electric conduction agent conversely, conductivity fell remarkably, and there was a problem that internal resistance became large.

[0004] Therefore, in fabricating a conductive thermoplastic film, it is necessary to balance conductivity and film reinforcement. Although 60-100 weight section addition needed to be carried out to the resin 100 weight section in order to acquire good conductivity when an electric conduction agent was made into acetylene black, when the moldability was taken into consideration, only 10 - 50 weight section extent could be added, and a volume-resistivity value was not able to be made not much low. Moreover, although 20 micrometers or less were desirable since thickness also covered a high volume-resistivity value, the present condition was that only an about at most 30-100-micrometer film is obtained on the problem of shaping, and conductivity does not become high to a request. When it was filled up with carbon black so much in consideration of conductivity and thickness was moreover made into 20-

micrometer level by coating, mechanical strengths ran short and there was also a problem that became easy to produce a tear, a piece, etc. and the yield of a product fell remarkably at the time of thermocompression bonding.

[0005]

[Problem(s) to be Solved by the Invention] In the conductive film for current collection on which the solid content polarity electrode used for an electric double layer capacitor is stuck, the purpose of this invention is examining wholeheartedly the ingredient of this conductive film for current collection, a presentation ratio, a process, etc., its volume-resistivity value is low, it has the mechanical strength which neither the tear at the time of thermocompression bonding nor a piece produces, is excellent in adhesion with a polarizable electrode, and is to offer the low conductive film for current collection of contact resistance.

[0006]

[Means for Solving the Problem] This invention is the charge collector film for electric double layer capacitors which used the drainage system electrolytic solution. The laminating of the conductive resin layer which consists of resin and an electric conduction agent is carried out to the side which touches a metal film with an electrode at least. Resin with urethane resin, acrylic resin, polyester resin, vinyl acetate resin, those copolymers, or those mixture A gel molar fraction has 90% or more of structure of cross linkage. An electric conduction agent And carbon black Or 10-500 weight section addition of the electric conduction agent is carried out to the resin 100 weight section with the fine particles or the fiber of Cu, Zn, and Au, and it is the conductive film for charge collectors whose specific resistance of a conductive resin layer is 1 or less ohm-cm. It is the conductive film for charge collectors whose metal film the thickness of a conductive resin layer is 1-10 micrometers of one side at least, and is either aluminum or Cu preferably and whose thickness is 10-30 micrometers.

[0007]

[Embodiment of the Invention] This invention is the system to which the specific resistance which has sulfuric-acid-proof nature on the conductive film for charge collectors at the side which touches an electrode at least carried out the laminating of the conductive resin layer below 1ohm and cm to the metal film of 10-30-micrometer thickness by the thickness of 1-10 micrometers. These ingredient classes, a presentation ratio, and a process are compared with conventional electroconductive glue and a conventional conductive thermoplastic film by inquiring wholeheartedly. A volume-resistivity value is low, and it has the mechanical strength which neither the tear at the time of thermocompression bonding nor a piece produces also with the thin film which is 10-50 micrometers, excels in adhesion with a polarizable electrode, and came to complete from the knowledge which can obtain the low conductive film for current collection of contact resistance. If the reason for having chosen this construct here is explained, a metallic foil will bear about the conductivity to the thickness direction of a charge collector, and surface conductive resin will reduce contact resistance with an electrode sharply, and the resistance to the sulfuric-acid electrolytic solution will be given, and it will be mentioned that it can be satisfied with the point in which adhesion with a gasket is possible of conductivity equivalent to a metal, the chemical resistance of resin, and an adhesive property at coincidence.

[0008] As for the conductive resin layer, it is better to carry out the double-sided laminating of it preferably, if it takes prospective double-sided electrode-ization etc. into consideration although the conductive film used for this invention is the system which carried out the laminating of the conductive resin on the metal film, and one side by the side of an electrode is the minimum need.

[0009] Urethane, an acrylic, polyester, vinyl acetate, etc. are used for the base resin of conductive resin, and it is desirable that the bridge is constructed. However, as long as there is resistance over a sulfuric-acid water solution, in the condition of thermoplastic resin is sufficient. To make bridge formation give sulfuric-acid-proof water-solution nature, 90% or more of a gel molar fraction is required. Sufficient sulfuric-acid-proof water-solution nature is not obtained by less than 90% of case.

[0010] Moreover, contact resistance increases and the specific resistance of conductive resin cannot attain low resistance-ization, if 1 or less ohm-cm is required and exceeds this. Furthermore, 1-10 micrometers per each class are suitable for the thickness of an electric conduction resin layer, and it is 1-

5 micrometers preferably. In less than 1 micrometer, sufficient sulfuric-acid-proof water-solution nature will not be obtained, but, in the case of aluminum etc., an inner metal film will corrode. Moreover, when exceeding 10 micrometers, a resin layer will become weak, and a crack or peeling will be produced in the handling in an electric double layer capacitor production process.

[0011] The electric conduction agents used for this invention are powder or fibers, such as carbon black, such as acetylene black and KETCHIEN black, and Cu, Zn, Au, and its use of KETCHIEN black is more desirable than conductivity desirable and good at little addition is acquired. An electric conduction agent carries out 10-500 weight section addition to the resin 100 weight section. Preferably, it is the 20 - 150 weight section. Good conductivity with an addition deficient in the addition effectiveness in under 10 weight sections is not acquired. Moreover, since the poor dispersibility of an electric conduction agent may be caused or the mechanical strength of a film may be insufficient if the 500 weight sections are exceeded, it is not desirable.

[0012] Moreover, as a metal film in a charge collector, they are aluminum or Cu. Preferably, aluminum foil is good also from a cost side. The thickness of this metal film is 10-30 micrometers, and its 10-20 micrometers are preferably good. In less than 10 micrometers, there is a danger of a metal film being too thin and generating Siwa and a tear during electric double layer capacitor assembly. If 30 micrometers is exceeded, film weight will be heavy and will lead also to a cost rise.

[0013]

[Example] Next, one example of this invention is shown. However, this invention is not limited to the following examples and the manufacture approach is also conventionally possible for it also by the well-known melting producing-film method.

Distributed mixing of the polyurethane resin 100 weight section of the <example 1> molecular weight 1 million, the electric conduction agent KETCHIEN black 50 weight section, the isocyanate 5 weight section, and the toluene 480 weight section was carried out in the ball mill for 24 hours, and the conductive paint was obtained. Double spread desiccation of this conductive paint was carried out so that the thickness after desiccation might be set to 2 micrometers with a doctor blade method on 20micromAl foil base material which performed the surface roughening process, and the three layer conductivity film of current collection body and its function was obtained. The average internal resistance value at the time of producing the volume-resistivity value of the obtained film and ten primitive cells of the electric double layer capacitor shown in drawing 3, the tear at the time of thermocompression bonding, and the existence of a piece were evaluated. A result is shown in Table 1.

[0014] The three-layer coating film was obtained by the same approach as an example 1 by the combination formula shown in the <examples 2-5> table 1, and the conductive film for charge collectors was produced. The result of having performed the same measurement as an example 1 using the obtained film is shown in Table 1.

[0015] With the extrusion method, melting film production of the masterbatch which carried out mixed distribution of the acetylene black 50 weight section at the <example 1 of comparison> polypropylene resin 100 weight section was carried out so that it might become 50 micrometers in thickness, and the conductive film of the example of a comparison was obtained. The result of having performed the same measurement as an example 1 using the obtained film is shown in Table 2.

The melting film production film was obtained by the same approach as the example 1 of a comparison by the combination formula shown in the <examples 2-4 of comparison> table 2, and the conductive film for current collection was produced. The result of having performed the same measurement as an example 1 using the obtained film is shown in Table 2.

[0016] <Measuring method> Evaluation of fine adhesiveness stuck by pressure the charge collector films cut off in the shape of [ of 25mm width of face ] a strip of paper by the 2kg platen, performed 180-degree friction test after 20-minute progress, and used the thing with the peel strength of 10g / 25mm or more as the excellent article. About the gel molar fraction of conductive resin; the residual weight after immersion was measured into the after [ bridge formation ] xylene. From the obtained conductive film, specific resistance started the 50mmx20mm sample, and measured it using the four point probe method (RORESUTA AP: Mitsubishi Chemical, Inc. make). Average internal resistance added 1kHz and 1mA

to the primitive cell of the electric double layer capacitor shown in drawing 3, measured and computed the electrical potential difference of both ends, and used as the excellent article what has the internal resistance of 1ohm or less fundamentally. About existence, such as a tear, the front face of 50 primitive cells was observed and distinguished with the optical microscope.

[0017]

[Table 1]

項 目	実施例 1	実施例 2	実施例 3	実施例 4	実施例 5
(導電樹脂配合 重量部)					
ポリウレタン樹脂	100				100
アクリル樹脂		100			
ポリエステル樹脂			100		
ポリ酢酸ビニル樹脂				100	
ケッチェンブラック	50		30	20	40
アセチレンブラック		120			
Cuファイバー			40		
Zn粉末				70	
Au粉末					50
イソシアネート樹脂	5	5	5	5	5
導電樹脂層厚み [ $\mu\text{m}$ ]	10	10	10	10	10
粘着性 [ $\text{g}/25\text{mm}$ ]	53	31	22	20	20
ゲル分率 (%)	95	90	91	93	93
体積抵抗値 [ $\Omega \cdot \text{cm}$ ]	0.51	0.87	0.43	0.35	0.54
平均内部抵抗値 [ $\Omega$ ]	0.14	0.11	0.13	0.11	0.11
破れ等の有無	0/50	0/50	0/50	0/50	0/50

[0018]

[Table 2]

項 目	比較例 1	比較例 2	比較例 3	比較例 4
ポリエチレン樹脂	100	—	—	—
ポリプロピレン樹脂	—	100	100	100
アセチレンブラック	120	80	—	—
ケッチェンブラック	—	—	70	7
フィルム厚み [ $\mu\text{m}$ ]	40	50	20	50
粘着性 [ $\text{g}/25\text{mm}$ ]	密着せず	密着せず	密着せず	34
ゲル分率 (%)	—	—	—	—
体積抵抗値 [ $\Omega \cdot \text{cm}$ ]	5.54	7.75	4.34	5.70
平均内部抵抗値 [ $\Omega$ ]	7.09	10.5	3.16	22.0
破れ等の有無	10/50	7/50	25/50	0/50

[0019]

[Effect of the Invention] As compared with the conventional conductive thermoplastic film, as for the conductive film for current collection obtained by this invention, the conductivity which was excellent

also in the same thickness since the volume-resistivity value was low is acquired. Moreover, since it excels in the mechanical strength, even if thinner than the conventional conductive thermoplastic film, the tear at the time of thermocompression bonding and a piece can be prevented. Furthermore, since it has fine adhesiveness, it can excel in adhesion with a metal-electrode plate or a polarizable electrode, and contact resistance can be reduced, and the reduction of the internal resistance of an electric double layer capacitor and the improvement in the engine performance which were applied can also be aimed at.

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CLAIMS

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[Claim(s)]

[Claim 1] It is a charge collector film for electric double layer capacitors using the drainage system electrolytic solution. The laminating of the conductive resin layer which consists of resin and an electric conduction agent is carried out to the side which touches a metal film with an electrode at least. Resin with urethane resin, acrylic resin, polyester resin, vinyl acetate resin, those copolymers, or those mixture A gel molar fraction has 90% or more of structure of cross linkage. An electric conduction agent And carbon black, Or the conductive film for charge collectors which 10-500 weight section addition of the electric conduction agent is carried out to the resin 100 weight section, and is characterized by the specific resistance of a conductive resin layer being 1 or less ohm-cm with the fine particles or the fiber of Cu, Zn, and Au.

[Claim 2] The conductive film for charge collectors according to claim 1 whose thickness of a conductive resin layer is 1-10 micrometers of one side at least.

[Claim 3] The conductive film for charge collectors according to claim 1 or 2 whose thickness a metal film is 10-30 micrometers in either aluminum or Cu.

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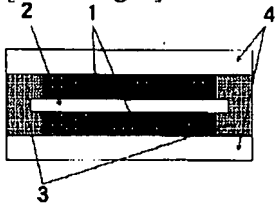
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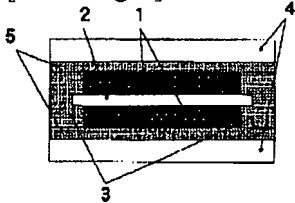
DRAWINGS

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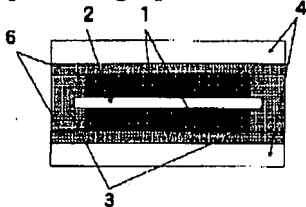
[Drawing 1]



[Drawing 2]



[Drawing 3]



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